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(71) Applicant: AMERICAN OPTICAL CORPORATION  
14 Mechanic Street  
Southbridge, MA 01550(US)

(72) Inventor: Leboeuf, Albert R.  
10 Shepard Road  
Sturbridge Massachusetts 01701(US)

(72) Inventor: Singer, Helmut K.  
11 Carolyn Terrace  
Southborough Massachusetts 01772(US)

(74) Representative: Popp, Eugen, Dr. et al,  
Patentanwälte Popp, Sajda, v. Bülow, Hrabal & Partner  
Widenmayerstrasse 48 Postfach 86 06 24  
D-8000 München 86(DE)

DOC

(54) Silicone-containing hard contact lens materials having increased oxygen permeability.

(57) This invention relates to an improved hard contact lens polymeric material comprising a siloxane-based ester monomer, solely, or in combination with methacrylic acid-derived cross-linking agents, alkanol esters, and/or hydrophilic monomers. Hard contact lenses made from these polymeric materials have an increased oxygen permeability and surface wettability and thus have potential use in extended-wear lens applications.

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# EUROPEAN SEARCH REPORT

0108886

Application number

EP 83 10 9141

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 8)
X	US-A-4 306 042 (R.A. NEEFE) * Claim 1 *	1-9	C 08 F 230/08 B 29 D 11/02 // (C 08 F 230/08 C 08 F 220/20 )
X	US-A-4 152 508 (E.J. ELLIS) * Claim 1 *	1-9	
X	US-A-4 246 389 (A.R. LEBOEUF) * Claim 1 *	1-9	
X	US-A-4 248 989 (N.N. NOVICKY) * Claim 1 *	1-9	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 8)
			C 08 F B 29 D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14-08-1984	Examiner CAUWENBERG C.L.M.
CATEGORY OF CITED DOCUMENTS.			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons	

1           SILICONE-CONTAINING HARD CONTACT LENS MATERIALS  
            HAVING INCREASED OXYGEN PERMEABILITY

BACKGROUND OF THE INVENTION

5           This invention relates to a siloxane-based  
hard contact lens material with improved gas permeability  
and surface wettability characteristics.

            Hard and soft contact lenses can correct  
visual defects such as myopia (nearsightedness) or  
10   hyperopia (farsightedness); but, both types of lenses  
have specific advantages and problems.

            Conventional hard contact lenses, first develop-  
ed in 1940, are made from polymethylmethacrylate (PMMA).  
Hard contact lenses have several advantages over conven-  
15   tional soft contact lenses; they have better visual  
acuity, can correct astigmatism, are less expensive,  
easier to care for, are more durable, and can be tinted,  
polished to remove scratches, or reground to make slight  
changes in prescription or fit. Hard contact lenses,  
20   however, have several problems or disadvantages: Several  
weeks are required for comfortable adjustment; and  
they must be worn almost daily to maintain this tolerance;  
and, they restrict oxygen flow to the cornea, because  
of low permeability, which can cause corneal edema  
25   or swelling, corneal infections, vascularization (growth  
of blood vessels into the cornea), or blurred vision.  
The cornea must be periodically allowed to recuperate  
and replenish its oxygen by removing the lens; thus,  
hard contact lenses of PMMA are unacceptable for extended-  
30   wear use. Hard PMMA contact lenses normally have an  
oxygen permeability range of 0.1-0.5 Barrier Units  
(BU).

            Soft contact lenses were developed to offset  
many of the problems associated with hard contact lenses  
35   and account for the majority of the contact lens market.  
Conventional soft contact lenses are generally made  
from hydrophilic polyhydroxy-ethylmethacrylate or hydro-

1 phobic silicon rubber. Advantages of soft contact  
lenses are: there is less sensation of a foreign body  
than with hard contact lenses, thus the wearer more  
readily adjusts to them; they do not irritate the eyelid  
5 and cornea as much because of their flexibility; and,  
they fit more snugly on the cornea keeping out much  
of the dust and particles which can cause discomfort  
to a hard-lens wearer. Soft contact lenses, however,  
are expensive, must be replaced more frequently because  
10 they are more fragile, require expensive daily lens  
care which is also time-consuming, become soiled during  
wear from tears circulating between the cornea and  
lens, and must be replaced if a new prescription or  
fit is required. Specific problems associated with  
15 silicon rubber soft contact lenses are: they tend to  
produce a burning sensation because they are hydrophobic  
and differ from the cornea in thermal properties, such  
as thermal conductivity and thermal diffusivity; they  
have very low strength; and, they make machining very  
20 difficult, due to their softness and elasticity. Conventional soft contact lenses are composed of up to 40%  
water by weight, which allows more oxygen flow to the  
cornea than a conventional hard contact lens. Even  
with this high water content, the oxygen flow to the  
25 cornea is insufficient for extended-wear applications.  
In addition, soft contact lenses may tend to shrink  
in a dry or heated environment because of this high  
water content, causing poor and fluctuating visual  
acuity, and eye irritation or vision blurring.

30 High-water content soft contact lenses composed  
of 60% to 90% water by weight have been developed for  
extended-wear use; but, even this increased amount  
of water is often insufficient in solving corneal respira-  
tion problems (lack of oxygen). Additionally, these  
35 lenses are fragile, expensive, must be cleaned periodical-  
ly because of a protein buildup from tears, have a  
lower visual acuity from shrinkage due to water evapora-

1 tion, and may discolor. Soft contact lens materials  
normally have the following oxygen permeability ranges;  
6-9 BU with a water content of 40%-45% by weight, 10-  
14 BU with a water content of 50%-60% by weight, and  
5 24-40 BU with a water content of 70%-90% by weight.

Hard contact lenses with an increased gas permeability, commonly known as gas-permeable lenses, have been developed to overcome problems associated with conventional hard and soft contact lenses. Gas-  
10 permeable contact lenses are generally made from cellulose acetate butyrate (CAB) or from a copolymer of PMMA and silicone. Gas-permeable lenses are durable, have high visual acuity, and as their name infers, allow oxygen to flow directly to the cornea. Prior  
15 art gas-permeable hard contact lenses, however, tend to have insufficient oxygen permeability for extended-wear applications.

#### SUMMARY OF THE INVENTION

20 To overcome many of the aforementioned problems associated with prior art hard and soft contact lenses, it is an object of this invention to provide a hard, gas-permeable contact lens material with an increased gas permeability (8-20 BU), good durability, compatibil-  
25 ity with corneal tissue, good visual acuity, and relative ease in machining, with potential use for extended-wear lens applications.

It is further object of this invention to increase the surface wettability characteristics of  
30 this contact lens material by the addition of reactive surfactants, thus making the lens more comfortable for wear.

According to the present invention, the improved contact lens materials comprise: 1) a copolymer of:  
35 a) about 15% to 40% by weight of tris (trimethylsiloxyl) methacryloxypropyl-silane (TRIS), b) about 10% to 80% by weight of at least one cross-linking agent which

1 is a derivative of methacrylic acid, and, c) about  
0% to 60% by weight of an alkanol ester and/or a hydro-  
philic monomer; or, 2) a homopolymer essentially of  
one of the following siloxane-based monomers: a) bis  
5 (methacryloxypropyl)octamethyltetra-siloxane (BMOS),  
a siloxane-based cross-linking agent, or, b) bis(meth-  
acryloxypropyl)tetramethyldisiloxane (MOTS), a siloxane-  
based cross-linking agent, or, c) methacryloxypropyl-  
pentamethyl-disiloxane (MPPS), a siloxanyl alkyl ester  
10 monomer.

Unique features of the siloxane-based ester  
monomers of this invention are; an enhanced fluid and  
gas transmission because of their specific permeable  
intermolecular structures, as well as a good chemical  
15 compatibility with corneal tissue. Surfactants used  
for the purposes of this invention, such as polyethylene  
glycol dimethacrylate (n=10-11, molecular weight=600),  
PEGDMA-600, and polyethyleneoxidedimethylsiloxane block  
copolymer: dimethacrylate, DMA/Q4-3667, modify the  
20 surface wettability of the copolymers which makes the  
lenses more comfortable for wear. Hydrophilic monomers  
used in this invention, such as 2-hydroxyethyl methacry-  
late (HEMA) and n-vinyl pyrrolidone (NVP) also increase  
the wettability of the polymer because of their inherent  
25 "hydrophilic" properties. Other monomers included  
in the materials of this invention act as modifiers  
to achieve desired levels of polymer flexibility or  
rigidity.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

30 The novel copolymer of the present invention  
preferably contains: a) 20% to 40% by weight of the  
siloxane-based ester monomer TRIS, b) 40% to 80% by  
weight of methacrylic acid-derived cross-linking agents,  
and, c) 0% to 20% by weight of an alkanol ester and/or  
35 a hydrophilic monomer.

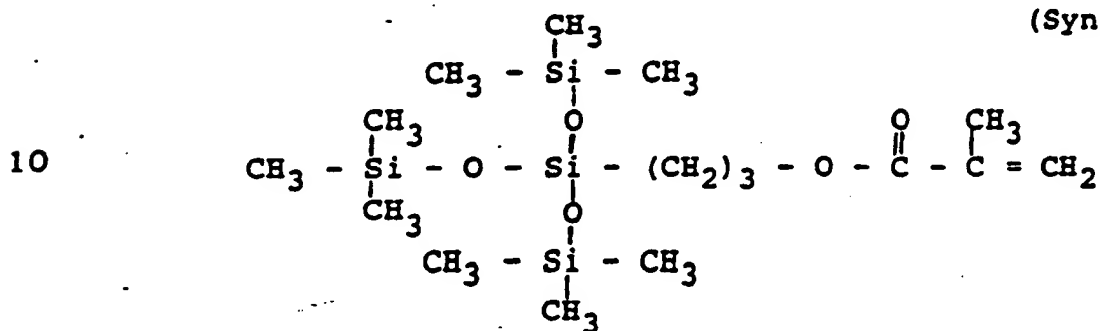
Novel homopolymers of the present invention  
preferably contain essentially 100% of either of the

- 1 following siloxane-based ester monomers: a) BMOS, or,  
 b) bis(methacryloxypropyl)tetramethyldisiloxane (MOTS),  
 or, c) MPPS.

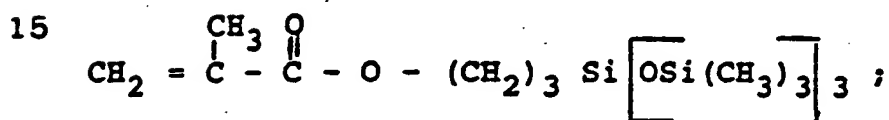
5 General structural formulas of the siloxane-based ester monomers are as follows:

tris(trimethylsiloxyl)methacryloxypropylsilane (TRIS)

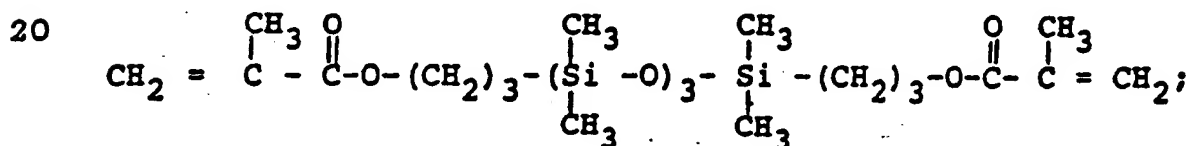
(Syn-17)



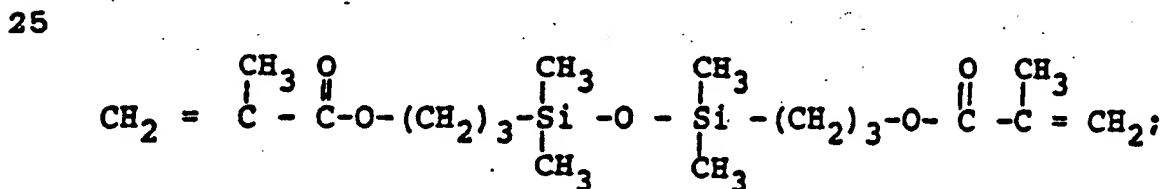
or



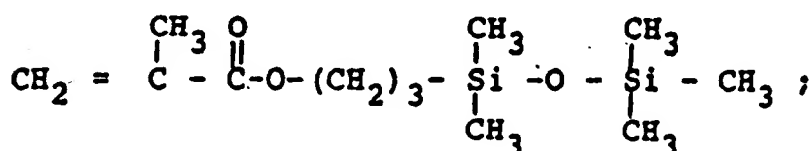
bis(methacryloxypropyl)octamethyltetrasiloxane (BMOS)



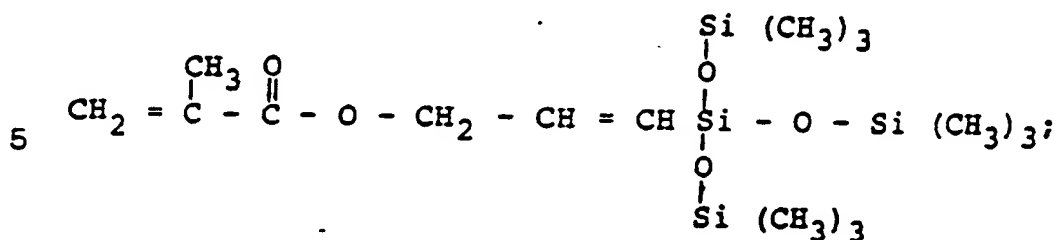
bis(methacryloxypropyl)tetramethyldisiloxane (MOTS)



30 methacryloxypropylpentamethyldisiloxane (MPPS)

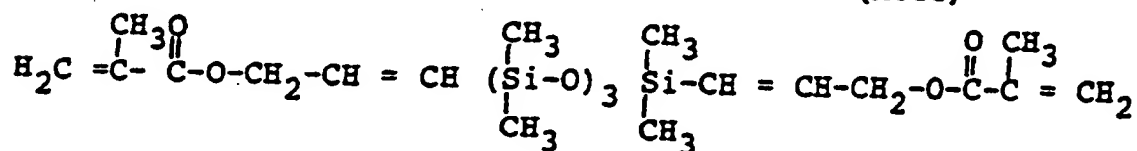


1 Tris(trimethylsiloxy)methacryloxypropargyl silane (TRIG)



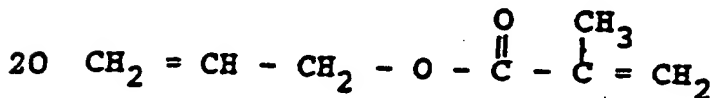
and

10 1,7 Bis(methacryloxypropargyl)octamethyl tetrasiloxane (MOTG)

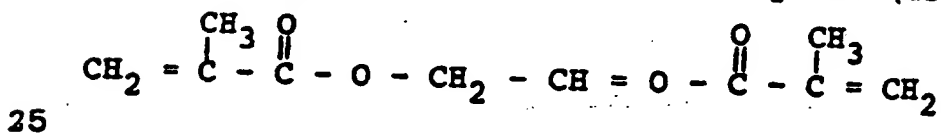


15 Representative cross-linking agents from methacrylic acids which may be used to form the copolymer of this invention include:

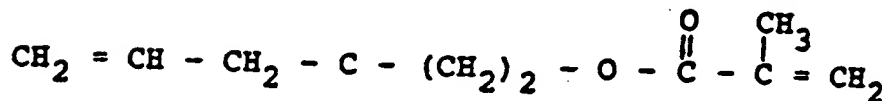
allyl methacrylate (AMA)



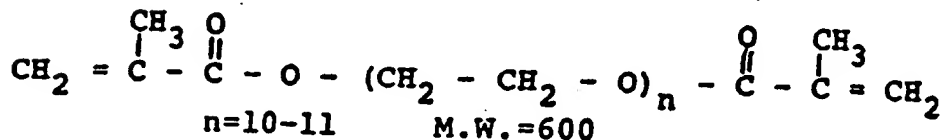
ethylene glycol dimethacrylate (EDMA)



2-allyloxyethyl methacrylate (HALEMA)



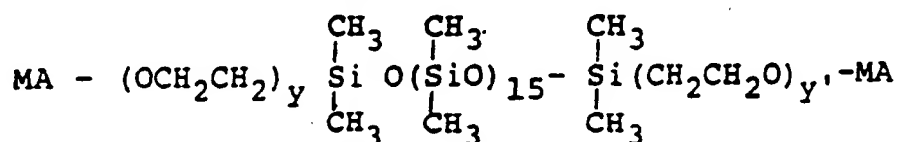
30 PEGDMA-600





1

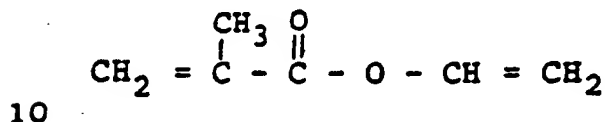
DMA/Q4-3667



5

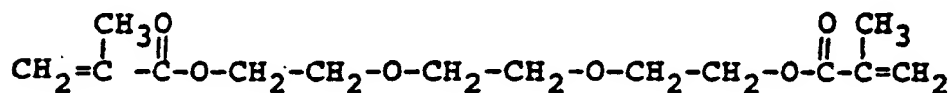
M.W. = 2524  $y + y' = 26$ 

vinyl methacrylate



10

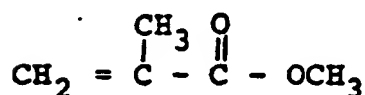
Triethylene glycol dimethacrylate (TREG)



15

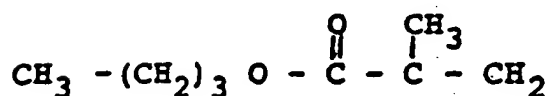
Representative alkanol esters which may be used to form the copolymer of this invention include:

methyl methacrylate (MMA)



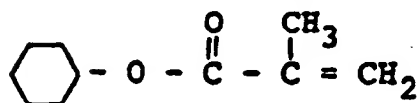
20

n-butyl methacrylate



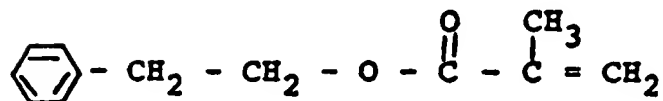
25

cyclohexyl methacrylate

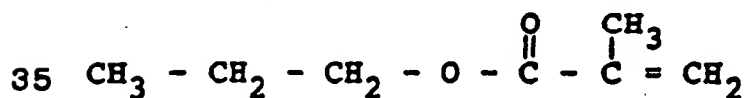


phenyl ethyl methacrylate

30



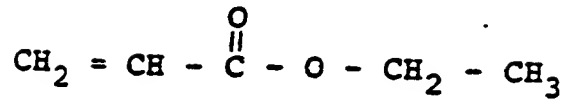
n-propyl methacrylate



35

1

Ethyl Acrylate



5

Other agents which perform the same function as the alkanol esters are vinyl benzenes such as:

Vinyl Benzene

10



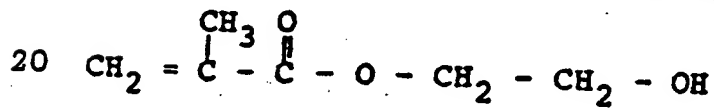
Divinyl Benzene



15

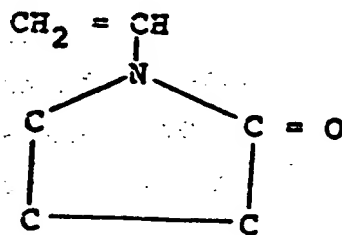
Representative hydrophilic monomers which may be used to form the copolymer of this invention include:

2-hydroxyethyl methacrylate (HEMA)



25

n-vinyl pyrrolidone (NVP)



Conventional polymerization techniques are used to produce the polymeric materials. Polymerization can be carried out in a lens mold to directly form the desired contact lens, or in a suitable mold to form sheets which may then be machined into the desired contact lens.

35

The invention is further illustrated by the following non-limiting examples.

1

Example 1

A monomer mixture is prepared by combining 40% by weight of TRIS, 40% by weight of allyl methacrylate and 20% by weight of n-propyl methacrylate. To this mixture is added 0.2% by weight of the above mixture of benzoin methyl ether and 0.5% by weight of t-butyl peroctate catalyst. The resulting mixture is placed in a polypropylene lens mold and irradiated for 30 minutes using a 3600 Å ultraviolet source at 4 inches, having a flux of 8400 watts/cm<sup>2</sup> at 18 inches. Castings are then postcured at a temperature of 100°C to 110°C for 1 to 2 hours in an air circulating oven. The resulting polymeric contact lens material contains 7% water by weight and has an oxygen permeability of 18 BU.

15

Example 2

The procedure of Example 1 is followed except that the starting monomer mixture contains 20.3% by weight of TRIS, 39.7% by weight of allyl methacrylate and 40.0% by weight of PEGDMA-600. The resulting polymeric contact lens material has an oxygen permeability of 8.3 BU.

Example 3

The procedure of Example 1 is followed except that the starting monomer mixture contains 19.9% by weight of TRIS, 40.0% by weight of PEGDMA-600, 35.0% by weight of HALEMA, and 5.1% by weight of n-propyl methacrylate. The resulting polymeric contact lens material has an oxygen permeability of 8 BU.

Examples 4-7

The procedure of Example 1 is followed except that the starting monomer mixtures contain the following constituents and proportions as listed in Table 1.

1

Table 1

Compositions and Proportions of Starting Monomers  
to Form Copolymer

5

Ex.	TRIS	NPMA	AMA	EDMA	PEGDMA			DMA/	
					-600	HEMA	NVP	Q4-3667	HALEMA
10	4	29.5	29.7	29.9	10.8	-	-	-	-
									(SUM=99.9)
	5	22.9	31.1	-	-	18.0	18.0	10.0	-
	6	24.7	34.5	-	-	34.5	-	-	6.4
15									(SUM=100.1)
	7	30.3	35.1	-	-	-	-	-	34.5
									(SUM=99.9)

20 TRIS=tris(trimethylsiloxyl)methacryloxypropylsilane

NPMA=n-propyl methacrylate

AMA=allyl methacrylate

EDMA=ethylene glycol dimethacrylate

25 PEGDMA-600=polyethylene glycol dimethacrylate (n=10-11,  
molecular weight=600)

HEMA=2-hydroxyethyl methacrylate

NVP=n-vinyl pyrrolidone

DMA/Q4-3667=polyethyleneoxide dimethylsiloxane block  
copolymer:

30 dimethacrylate

HALEMA=2-allyloxethyl methacrylate

Example 8-14

The procedure of Example 1 is followed except  
that the starting monomer mixtures contain the following  
35 constituents and proportions as listed in Table 2.

1

Table 2

Compositions and Proportions of Starting  
Monomers to Form Copolymer

5

Ex.	PEGDMA				DMA/Q4						
	TRIS	-600	PHEMA	VMA	AMA	3667	NVP	EDMA	HALEMA	MNA	
10	8	30.0	10.0	60.0	-	-	-	-	-	-	-
	9	20.2	39.7	-	40.0	-	-	-	-	-	-
											(SUM=99.9)
15	10	29.5	20.5	-	-	0.3	14.8	34.9	-	-	-
	11	20.0	39.5	-	-	20.5	-	-	20.0	-	-
	12	20.3	40.3	-	-	-	-	-	40.9	-	-
											(SUM=101.5)
20	13	25.0	35.1	-	-	-	-	-	-	39.9	-
	14	30.0	39.8	-	-	-	-	-	-	-	30.2

25 TRIS=tris(trimethylsiloxyl)methacryloxypropylsilane  
PEGDMA-600=polyethylene glycol dimethacrylate (n=10-11,  
molecular weight=600)

PHEMA=phenyl ethyl methacrylate

VMA=vinyl methacrylate

30 AMA=allyl methacrylate

DMA/Q4-3667=polyethyleneoxide dimethylsiloxane block  
copolymer:

dimethacrylate

NVP=n-vinyl pyrrolidone

35 EDMA=ethylene glycol dimethacrylate

HALEMA=2-allyloxyethyl methacrylate

MMA=methyl methacrylate

1

Examples 15-17

The procedure of Example 1 is followed except that the starting monomer mixtures contain the following constituents and proportions as listed in Table 3.

5

Table 3

Compositions and Proportions of Starting Monomers to Form Copolymer

10

	<u>Example</u>	<u>TRIS</u>	<u>TREG</u>	<u>AMA</u>	<u>PHEMA</u>	<u>MMA</u>
	15	49.8	25.7	24.4	-	-(SUM=99.9)
15	16	49.3	24.4	-	26.2	-(SUM=99.9)
	17	33.1	24.9	-	-	42.0

20 TRIS=tris(trimethylsiloxyl)methacryloxypropylsilane  
 TREG=triethyleglycol dimethacrylate  
 AMA=allyl methacrylate  
 PHEMA=phenyl ethyl methacrylate  
 MMA=methyl methacrylate

25

Example 18

The procedure of Example 1 is followed except that the starting monomer mixture contains 100% by weight of BMOS. The resulting polymeric contact lens material contains 1.7% by weight water and has an oxygen permeability of 20 BU.

30

Example 19

The procedure of Example 1 is followed except that the starting monomer mixture contains 100% by weight of MOTS bis(methacryloxypropyl)tetramethyldisiloxane. The resulting polymeric contact lens material has an oxygen permeability of 9.5 BU.

35

1

Example 20

The procedure of Example 1 is followed except  
that the starting monomer mixture contains 100% by  
weight of MPPS. The resulting polymeric contact lens  
5 material has an oxygen permeability of 21 BU.

Although the invention has been described  
with reference to its preferred embodiments, other  
embodiments can achieve the same results. Variations  
and modifications of the present invention will be  
10 obvious to those skilled in the art and it is intended  
to cover in the appended claims all such modifications  
and equivalent as follows in the true spirit and scope  
of this invention.

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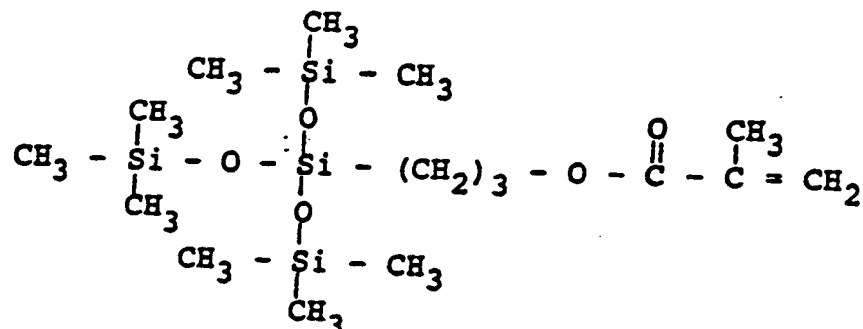
What is claimed is:

1. An oxygen-permeable, hard, machinable contact lens material comprising the polymerization product of:

5

(a) 15% to 40% by weight of tris(trimethylsiloxy)methacryloxypropylsilane (TRIS), having the following structural formula:

10



15

(b) 10% to 80% by weight of at least one cross-linking agent which is a derivative of methacrylic acid, and;

(c) 0% to 60% by weight of an alkanol ester and/or vinyl benzene and/or a hydrophilic monomer.

20

2. A polymerization product in accordance with claim 1 wherein said cross-linking agents in (b) are selected from the class consisting essentially of allyl methacrylate, ethylene glycol dimethacrylate, 2-allyloxyethyl methacrylate, PEGDMA-600, DMA/Q4-3667, vinyl methacrylate and triethylene glycol dimethacrylate.

25

3. A polymerization product in accordance with claim 1 wherein said alkanol ester in (c) is selected from the class consisting essentially of methyl methacrylate, n-butyl methacrylate, cyclohexyl methacrylate, phenyl ethyl methacrylate, and n-propyl methacrylate and said vinyl benzene is selected from a member of the group of vinyl benzene and divinyl benzene.

30

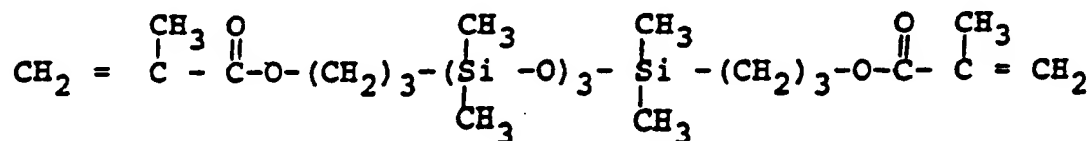
4. A polymerization product in accordance with claim 1 wherein said hydrophilic monomer in (c) is selected from the class consisting essentially of 2-hydroxyethyl methacrylate and n-vinyl pyrrolidone.

35



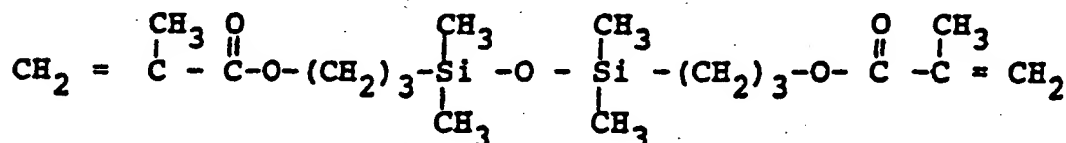
- 1 5. An oxygen-permeable, hard, machinable  
 contact lens material comprising the polymerization  
 product of bis(methacryloxypropyl)octamethyltetrasiloxane  
 (BMOS) having the following structural formula:

5

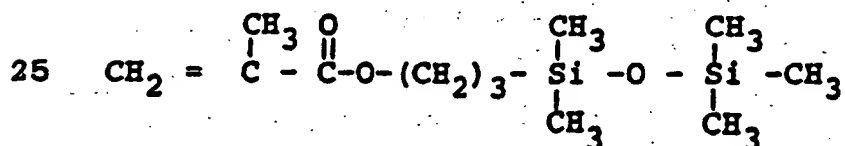


- 10 6. An oxygen-permeable, hard, machinable  
 contact lens material comprising the polymerization  
 product of bis(methacryloxypropyl)tetramethyldisiloxane  
 (MOTS) having the following structural formula:

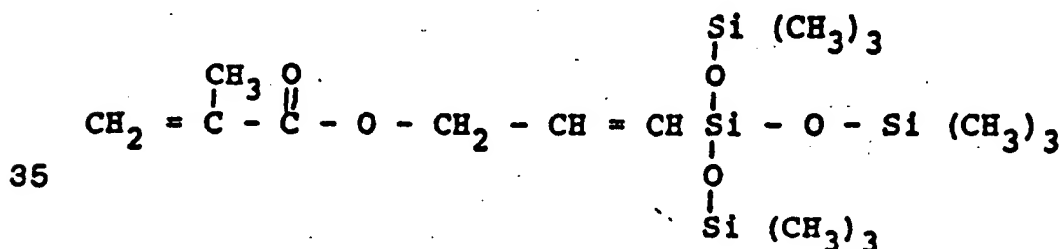
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- 20 7. An oxygen-permeable, hard, machinable  
 contact lens material comprising the polymerization  
 product of methacryloxypropylpentamethyldisiloxane  
 (MPPS) having the following structural formula:



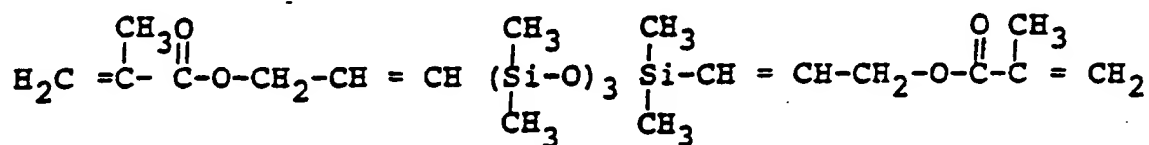
- 30 8. An oxygen-permeable, hard, machinable  
 contact lens material comprising the polymerization  
 product of tris(trimethylsiloxy)methacryloxypropargyl  
 silane (TRIG) having the following structural formula:



1

9. An oxygen-permeable, hard, machinable  
 contact lens material comprising the polymerization  
 product of 1,7 Bis(methacryloxypropargyl)octamethyl  
 tetrasiloxane (MOTG) having the following structural  
 formula:

5



10

15

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25

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35